SPECTRUM OF THE FLAME ABOVE A COPPER ARC IN AIR

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Plate III

ABSTRACT. The spectrum of the flame above a copper arc in air has been photographed on a glass prism spectrograph with a dispersion of about 12 Å per mm at λ5500Å, and all the radiations between λ4800 and λ6400 Å have been measured. A large number of bands exist. The origin and structure of most of them do not seem to be very well understood. A tentative arrangement for three systems of bands is given.

INTRODUCTION

The spectrum of the flame above a copper arc in air does not seem to have received the attention it deserves, by virtue of being associated with such a common source of radiation in a spectroscopic laboratory. It is believed that the radiation of the flame is chiefly due to CuO which has an intense system of band in the orange and red region and some weak bands in the green. Several measurements of the orange and red bands have been published (Mulliken, 1925; Mahanti, 1930; Loomis and Watson, 1935; Pearse and Gaydon, 1941; Rosen, 1945 and Guntsch, 1946), and some of these workers have also attempted an analysis of them, each in his own way. As for the bands in the other regions there does not seem to exist even a complete measurement of them (Hertenstein, 1912, Pearse and Gaydon, 1941; Rosen 1945; Lejeune and Rosen, 1945 and Rao, 1946) It was, therefore, considered necessary to photograph the spectrum of this flame and to make a complete measurement of the wavelengths of all the radiations present in it. This has been done and as a result it has been found that the spectrum is quite complicated and the structures are not easily understood. Full details are given in the following sections:

EXPERIMENTAL

The copper arc used was run from 110 volts D. C. supply. The electrodes were horizontal and the image of the flame above the level of the electrodes was thrown by means of a lens over the slit of a glass Littrow spectrograph having a dispersion of about 12 Å per mm. at λ5500 Å. Exposures of about one and a half hours on Ilford Special Rapid Panchromatic plates were necessary to get the fainter bands with an intensity so that they could be read in the microscope. The iron arc was used for comparison. A copper arc was also exposed side by side in order to eliminate the copper lines from the spectrum of the flame.

DESCRIPTION OF THE SPECTRUM

The spectrum of the flame is given in Plate III. The prominent features of the spectrum are the very intense bands in the orange region, one or two intense bands in the green, a large number of comparatively faint bands in the orange, yellow and green and the strong green and yellow lines of copper, which could not be eliminated, although their relative intensities have been considerably reduced The fainter bands can apparently be put into several groups described below

Beginning from the short wavelength side, the first group starts at λ4828Å and extends up to λ4916Å There are 9 prominent bands in this region with heads at λλ4828.5, 4836.5, 4845, 4852.5, 4862.5, 4871 5, 4882.5, 4893.5 and 4916Å. The last band is the most intense of the lot, although the others also are quite strong. The fainter bands of this group have heads at λλ4852 5, 4876, 4901, 4904 and 4911Å.

The second group lies between λ4976 and λ5040Å. Two bands at λλ5030 3 and 5039.5Å have distinct heads, both degraded to the red. The bands at λλ4976.1, 4982 7 and 4989 6Å are somewhat less intense These are also degraded to the red. There is a strong band at λ4996Å This is quite broad and does not show any head The measurement corresponds to the centre of the band. It is possible that there may be a faint structure at λ5002 Å which is masked by the above band. The other faint structures are at λλ5005.9, 5008.7 and 5011.9Å.

A single intense band lies at λ5071 4Å. It is degraded to the red but is quite blurred Another intense band occurs with head at λ5227.8Å, degraded to the red.

A third group starts at λ5274Å, 4 distinct bands appear with heads at λλ5274 0, 5278.9, 5282 7 and 5285.6Å. They all appear degraded to the red, but they are all so narrow that they look more or less like lines There are faint band heads at λλ5302 6 and 5304.6Å, followed by two stronger ones at λλ5307.4 and 5312 0Å

Again there are two bands, comparatively isolated, the intense one with head at λ5345.1 Å and the faint one, at λ5347.9 Å.

A fourth group of bands appears between λ5150 and λ5500Å. Nine heads have been measured, which seem to be gradually converging towards the short wavelength side They all appear degraded to the red The more prominent amongst them have their heads at λλ5496.1 and 5488 2Å. The others follow at shorter wavelengths with gradually decreasing separation and intensity.

A moderately intense band is observed at λ5529.5Å., degraded towards the red. Another one which is a little blurred appears at about λ5557Å

A fifth group of bands is observed between λ5827 and λ5895Å. Some of the bands of this group are blurred. The stronger and more distinct ones are at λλ5847.6 and 5856.0Å.

TABLE I

Wavelengths of bands in the flame above a copper arc in air.

λ_{air}(Å)	ν_{vac}(cm^{-1})	Int.	λ_{air}(Å)	ν_{vac}(cm^{-1})	Int
4828.4	20704.5	s	5833.3	17138.2	m
36.5	670.4	s	41.9	113.0	w
45.2	633.2	s	43.4 }	108.6 }	
52.6	601.8	s	47.6 }	096.3 }	m
54.9	592.0	m	50.4	088.1	?
62.4	560.2	s	56.0	071.8	m
65.7	546.3	w	59.6	063.0	w
71.4	522.3	s	66.0	042.7	m
75.8	503.7	m	73.7	020.3	w
82.6	475.2	s	80.3	001.2	w
89.1	448.0	w	89.1	16975.8	m
93.5	420.6	s	95.0	958.8	m
4901.0	398.3	w	5932.6	879.8	w
04.2	385.0	m	26.4	869.0	w
10.9	357.2	m	32.2	852.5	m
16.2	335.3	vs	36.0	841.7	w
76.1	090.5	w	40.5	828.9	m
82.7	063.9	m	43.6	820.2	vw
89.6	036.1	m	48.2	807.2	m
95.7	011.6	s	50.5	800.7	w
5002.6	19984.0	w	57.5	780.9	m
05.9	970.9	w	65.0	759.8	m
08.7	959.7	w	6030.1	578.1	?
11.9	947.0	m	45.1	537.8	vvs
30.3	874.0	s	46.6	535.3	?
39.5	837.7	s	48.3	529.0	s
71.4	712.0	vs	52.7	517.0	s
5227.8	123.2	vs	59.1	499.5	vvs
32.4	106.4	m	64.1	485.9	w
34.3	099.4	s	69.0	472.6	w
35.8 }	094.0 }	s	78.2	447.7	w
36.5 }	091.4 }		6146.8	264.1	vvs
41.8	072.1	vvs	51.1	252.8	w
74.0	18955.7	s	57.3	236.4	m
78.0	938.1	s	61.5	225.3	vvs
82.7	924.5	s	68.7	206.4	m
85.6	914.1	w	74.5	191.2	w
92.6	889.7	m	91.5	146.7	vw
5302.6	853.4	?	6205.3	110.8	w
04.6	846.3	w	11.6	094.5	w
07.4	836.4	m	20.1	072.5	m
12.0	820.1	vs	23.0	065.0	m
45.1	703.5	s	70.3	15943.8	w
47.9	693.7	?	80.1	918.9	w
5385.0	18565.0	?	89.1	896.1	w
5457.7	317.7	w	94.0	883.8	vvs
66.1	289.5	w	97.6	874.7	s
68.7	280.8	w	6302.6	862.1	m
72.7	267.5	w	13.5	834.7	m
77.0	253.1	m	23.9	808.7	w
82.2	235.8	m	78.5	674.3	w
88.2	215.9	m	84.9	657.6	vw
96.1	189.7	m	92.5	630.1	vw
5529.5	079.8	s	6400.3	620.0	s
56.8	17991.0	m	03.5	612.2	vw
57.9	987.4	s	15.2	583.7	vw
5827.6 }	155.0 }		30.2	547.3	vw
29.0 }	150.9 }	m			

A sixth group of bands appears between λ5922 6 and λ5965Å. This group of bands is followed by the very strong bands in the orange and red regions extending up to λ6550Å. Our measurements in this region are in general agreement with those due to Pearse and Gaydon (1941). The bands are degraded to the red. The structure is complex, consisting of several heads of varying intensity

A complete list of all wavelengths measured is given in Table I, and can be generally taken to be correct to within ±.1Å.

The intensities given are visual estimates, and the notations in that column have the following significance: *s* means strong, *m* means medium, *w* means weak, *v* means very and ? means that the band measured was so faint that its existence is doubtful. Measurements included in braces mean that the corresponding bands did not clearly indicate which way they were degraded and in such cases either both the ends and the centre or at least both tl have been measured. All the other bands were degraded to the red.

DISCUSSION

We will consider the strong bands in the red and orange and the fainter ones dispersed over the entire yellow and green regions separately.

(*a*) *Bands in the orange and red regions.* An analysis of the bands in this region was proposed by Mahanti (1930), but this is doubted by Loomis and Watson (1935). Rosen (1945) carried out a vibrational analysis of these bands and found that they could be represented by the equation,

$$\nu = 16222 - 625\ v'' + 3\ v''^2 + 274\ v'$$

A different equation for the vibrational analysis of these bands has been proposed by Guntsch (1946). According to him

$$\nu_0 = 16273.9 + 285\ 6u' - 9.2\ u'^2 - 318.6\ u'' + 4.4\ u''^2, \text{ where } u = v + \tfrac{1}{2}$$

Guntsch gives evidences in support of his equation He has also carried out the rotational analysis for 5 bands of this system and believes them to be due to $^2\Sigma - ^2\Sigma$ transition of CuO molecule. The *B* values are $B''_e = 0.632$ and $B'_e = 0\ 591\ cm^{-1}$. Our own arrangements, as given in Table II, is in agreement with Guntsch's equation, but it suffers from certain defects, *viz*, (1) the agreement is not as good as could be expected, (2) the vibrational differences are not very satisfactory and (3) all the bands in the region are not accounted for by this arrangement.

(*b*) *Bands in the green and yellow regions.* Although some of the measurements given in Table I in the yellow region may be associated with the orange bands, it seems doubtful if all of them can be accounted for in this way. Nor does there appear any clue for classifying the yellow and the green bands from an inspection of the spectrum. At any rate, then

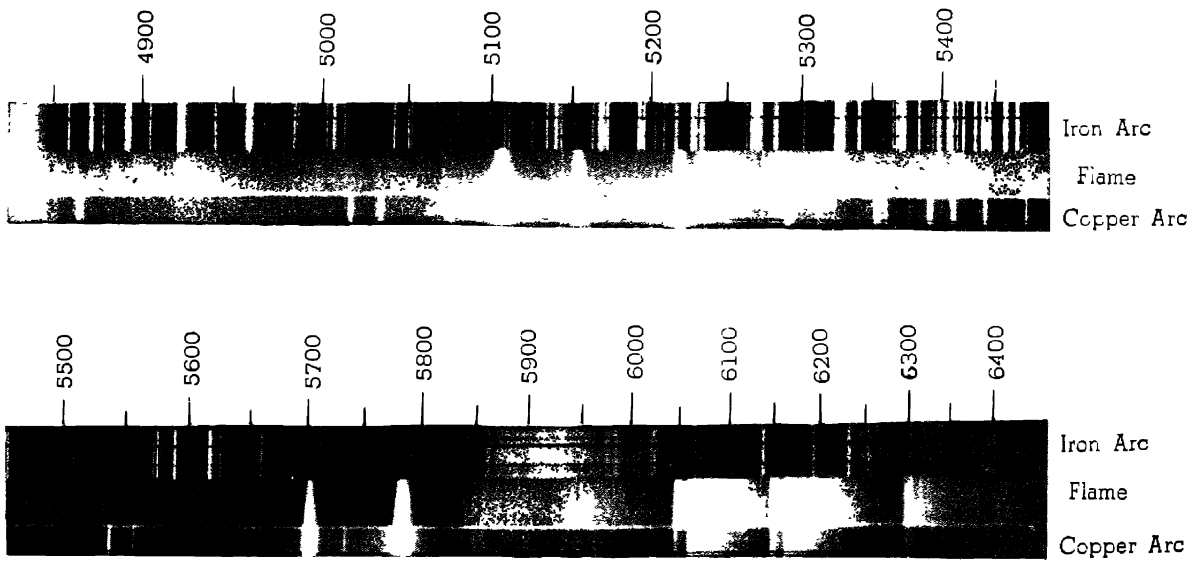

Fig 1.—Spectrum of the flame above a Copper arc in air

appearance is so different from that of the orange and red bands that it does not look probable that the entire stuff can be attributed to the same emitter. Yet certain bands, from their appearance, seem to suggest some sort of regularity. Thus the bands, referred to as belonging to the first group in the previous section, indicate, from their appearance, that it should be possible to arrange them in some sort of fragmentary system This is easily done, as given in Table III.

TABLE II

$v'-v''$ scheme for orange-red bands

v' \ v''	0	1	2	3	4	5
0	16264					
1	16538	6225	15920	15620	15310*	
2		16499		15884		15270*
						15547

Denotes that the corresponding band has been taken from Pearse and Gaydon (1941).

TABLE III

$v'-v''$ scheme for the bands between λ4828 and λ4916Å.

v' \ v''	0	1	2	3
0	20504	20385		
1	20592	20475	20357	
2	20670	20560	20448	20335
3		20633		20430

The ω's are, however, so much different from those suggested for the orange-red system by Guntsch that it is difficult to believe that those two systems are due to the same emitter.

The bands in the other groups mentioned in the previous section do not generally seem to suggest any order Some bands, however, between λ5270 and λ5530Å, can be picked up from the spectrogram and their separation indicated that they might belong to one system. Such bands are given in Table IV. This system may be attributed to the same emitter to which the orange system belongs, *i.e.*, to CuO. But here again none of the ω's agree and if both the systems belong to CuO, the states involved are all different.

TABLE IV

$v'-v''$ scheme for some bands in the green region.

v' \ v''	0	1	2	3	4
0	19093*	18821	18565	18318	18080
1		18956	18704		

* This band is strong, but its head is not distinct. The centre had to be measured.

More work seems necessary to clarify all these points.

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PATNA.

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